Crystallization of Lithia-Silica Glasses at High Pressure (Special Issue on Physics and Inorganic Chemistry)

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Crystallization of Lithia-Silica Glasses at High Pressure

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The powdered lithia-silica glasses of the compositions, $Li_2O \cdot 1.5SiO_2$, $Li_2O \cdot 2SiO_2$ and $Li_2O \cdot 4SiO_2$, were loaded to various pressures reaching to 30 kilobar (Kb) with the uniaxial high-pressure apparatus, and the crystalline phases produced in the glasses, the crystallization temperatures and the stability of the crystallization products were investigated. In all of the glass samples, lithium metasilicate crystals and silica crystals (quartz or coesite) were found to be produced by the application of high-pressures in place of lithium disilicate crystals, which precipitate at atmospheric pressure. The crystallization temperature of the glasses was greatly lowered by the application of high-pressure. The crystallization of the glasses was markedly enhanced by the presence of water. The lithium metasilicate-coesite mixtures produced from the $Li_2O \cdot 2SiO_2$ glass changed, when heated at atomospheric pressure, first into lithium metasilicate-quartz mixtures at the temperature from 750°C to 850°C and then into lithium disilicate crystals at the temperature from 900°C to 950°C.

I. INTRODUCTION

After the new high-pressure polymorph of silica, "coesite", was discovered by Coes[1], many studies have been made of synthesis and transformation of high-pressure modifications of silica and silicates. Some of these deal with the process of crystallization of silicate glasses. Roy *et al*,[2,3] made systematic studies of the effects of high-pressure on the rate of crystallization of glasses with various compositions: Zeto, Dachille and Roy[2] confirmed experimentally that the crystallization rate of SiO_2 glass is markedly increased by the application of high-pressure in excess of 10 kilobar (Kb) and also by the presence of water vapor. Blinov and Roy[3] studied the crystallization of glasses of the system, Li_2O-Al_2O_3-SiO_2, under the pressures up to 100 Kb and at temperatures up to 800°C, and found that eucryptite-and spodumen-composition glasses are converted, by application of pressures as low as 10 Kb, to various crystals which can not be obtained under the same time-temperature conditions.

The high-pressure experiments of Roy *et al*, were made by using the opposed-anvil type apparatus by which the pressure involving a fairly high degree of shear are applided to the specimens[4]. Using the high-pressure apparatus which generates the pressure of near hydrostatic nature, Eppler, Giardini and Tyding[5] obtained the results which contradict those of Roy *et al*,; i.e., the high-pressure decreased the rate of crystallization of the glass of the composition, Li_2O 20, Al_2O_3 10, and SiO_2 70 by weight percent.

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The present article deals with the effects of high-pressure on crystallization of a series of Li_2O–SiO_2 glasses, whose crystallization processes at atmospheric pressure were already well investigated by many researchers. At atmospheric pressure the glasses of this series crystallize at about 600°C[6], the precipitated crystalline phase being lithium disilicate for the glasses of silica rich compositions ($Li_2O \cdot 2SiO_2$, $Li_2O \cdot 3SiO_2$, $Li_2O \cdot 4SiO_2$, etc,) whereas lithium metasilicate and lithium disilicate for the glasses of low-silica composition ($Li_2O \cdot 1.5SiO_2$)[7].

The high-pressure apparatus used in the present experiment is of the uniaxial simple squeezer type previously used by the authors for the study of the refractive index changes of the glasses under high-pressure[8].

II. EXPERIMENTAL PROCEDURE

Preparation of Glasses

The molecular compositions of the glasses prepared were SiO_2, $Li_2O \cdot 4SiO_2$, $Li_2O \cdot 2SiO_2$ and $Li_2O \cdot 1.5SiO_2$. The SiO_2 glass samples were obtained from a commercial clear fused quartz (Toshibadenko Product; the coefficient of linear thermal expansion is 5.4×10^{-7}). The other glasses were prepared in the authors' laboratory. Batch materials used were lithium carbonate of high purity (Nippon Chemicals Product; the Li_2CO_3 content was over 99%) and potter's flint powders purified for use in manufacture of ordinary optical glasses. Batches to yield 100 gram glass were melted in platinum crucibles at 1370°~1420°C for 2 hours in an electric furnace with silicon-carbide heating elements. The melts were poured on a steel plate and, after cooled to room temperature, pulverized into powders of less 70 μ in diameter.

Application of High Pressure

The high-pressure appratus used consisted, essentially, of a high-pressure cell having a pair of symmetrically opposed cemented tungsten carbide pistons each embedded in a stellite holder, a 40 ton hydrostatic press and a split furnace with the nichrome resistance heater for external heating. The high-pressure cell is schematically shown in Fig. 1.

The application of high-pressure to the glass samples at high temperatures were conducted by the following procedure: The pulverized glass sample of about 0.3 gram was wrapped in a 0.02 mm-thick platinum foil, being placed between the opposed surfaces of the tungsten carbide pistons. Pressure was applied at room temperature up to about one thirds of the desired final pressure, and, under the pressure, the sample was raised to the desired temperature within about 20 minuites, the pressure was further increased to the final desired value. After the glass sample was compressed at the desired pressure and temperature for the desired duration, the split electric furnace was removed from a set of apparatus to allow the glass sample to cool. When the temperature of the sample fell to about 200°C the pressure was released. The cooling rate of the glass sample was fairly high; i.e., about 20°C/min. from 500° to 300°C, and about 15°C/min. from 300° to 200°C. In some experiments a drop of water was added to the sample powders wrapped in a platinum foil in order to investigate the effects of water on the

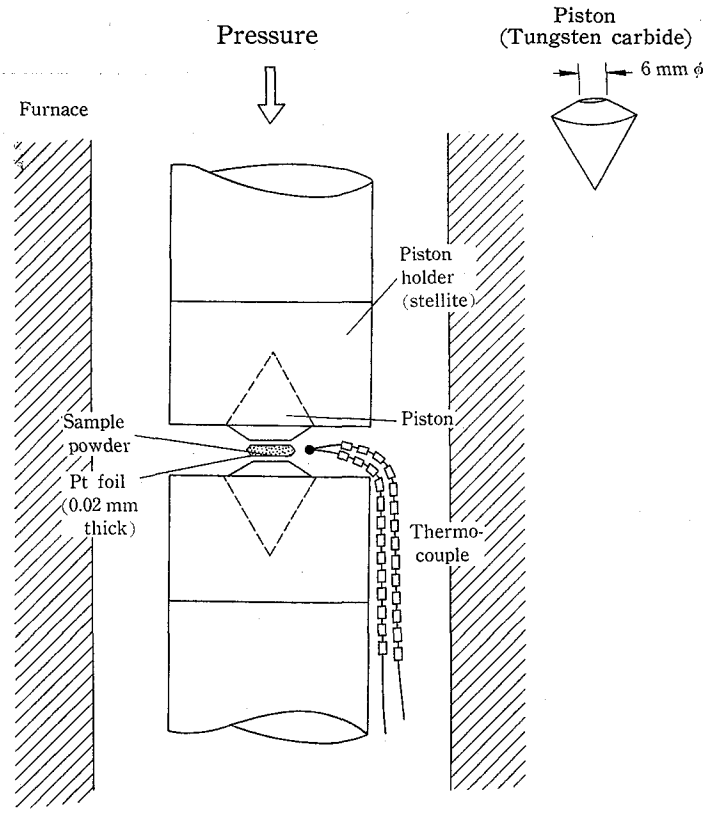

Fig. 1. High-pressure cell.

crystallization of the glass during compression. The temperature of the sample was measured by a chromel-alumel thermocouple mounted as shown in Fig. 1. In the present paper, the pressure applied to the sample was given in terms of total thrust divided by the cross sectional area of the piston.

The x-ray diffractometer used for the identification of crystals separated in the glass particles was of the type GX-2A of Shimadzu Co. with Cu Kα radiation.

III. EXPERIMENTAL RESULTS

Crystallization at High Pressures

(a) $Li_2O \cdot 2SiO_2$ glass

The results obtained with this glass are summerized in Table 1. The temperatures and pressures to which the samples were subjected, the crystals separated out in the glass powder and effects of addition of water are all given in the table. Durations of compression were 20 min. for all runs. Run was made only at the temperatures between 500° and 600°C. Below 500°C crystallization did not occure even under the pressure of 30 Kb. Over 600°C severe oxidation of the tungsten carbide pistons occured. Fig. 2 shows some examples of the X-ray diffraction patterns of the crystals precipitated in the compressed samples.

Table 1. Crystallization of $Li_2O \cdot 2SiO_2$ glass under high-pressure (duration of compression was 20 min).

Pressure (Kbar)	Temperature 500°C no water	500°C water added	550°C no water	600°C no water
0.001 (atm. pressure)	Glass	Glass	Glass	L2S
0.5	Glass	Glass	L2S (trace)	—
1	Glass	Glass	L2S+LS+Q	—
2	Glass	Glass	L2S+LS+Q	—
5	Glass	Glass	LS+Q	—
10	Glass	Glass	LS+Q	—
20	Glass	LS+Q	LS+Q+C (trace)	—
30	Glass	LS+Q	LS+C	—

Glass: Not crystallized L2S: Lithium disilicate crystal ($Li_2O \cdot 2SiO_2$)
LS: Liihium metasilicate crystal ($Li_2O \cdot SiO_2$) Q: Quartz (SiO_2) C: Coesite (SiO_2).

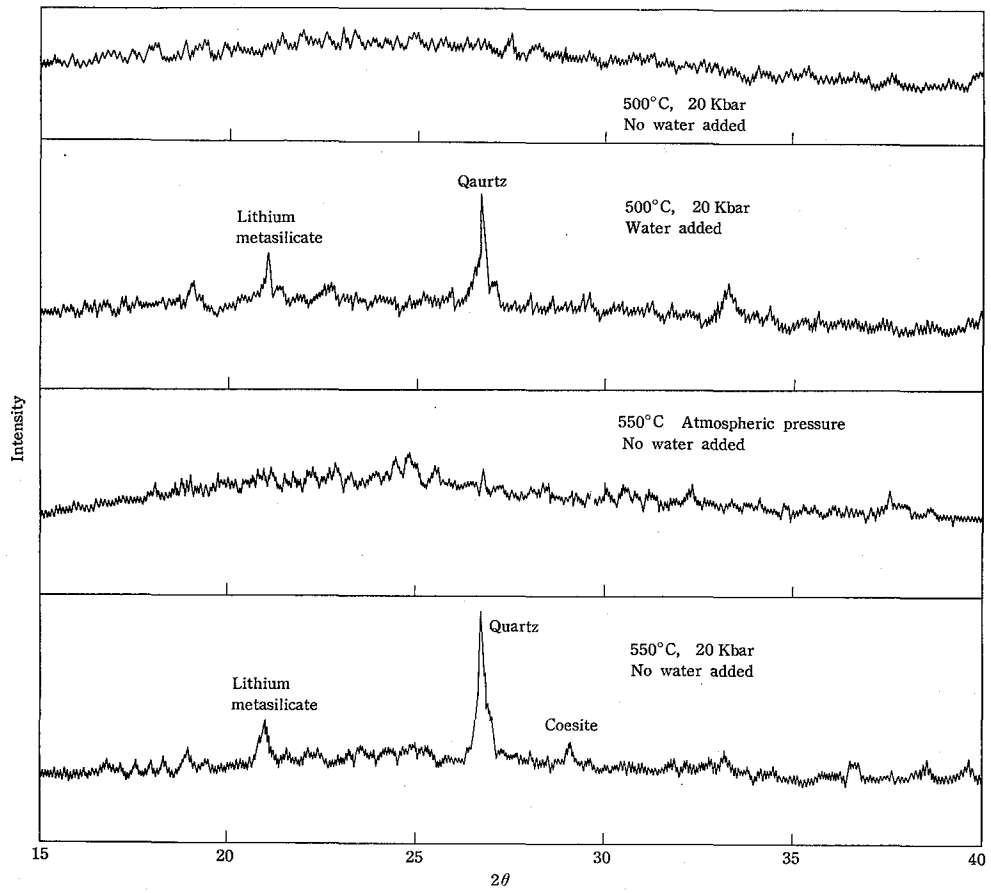

Fig. 2. X-rax diffraction patterns of $Li_2O \cdot 2SiO_2$ glass heat-treated.

From Table 1 and Fig. 2 it can be seen that the application of high-pressure increases the rate of crystallization of this glass, especially in the presence of water. The combined effect of pressure and water is seen for the runs made

at 500°C and at 20~30 Kb. In the presence of water, the $Li_2O \cdot SiO_2$ and quartz were found to crystallize out, whereas in the absence of water no crystals was observed.

The effect of pressure alone is seen for the runs made at 550°C. For both of the samples with and without water, the applications of pressures resulted in precipitation of various crystals in the glass samples: $Li_2O \cdot 2SiO_2$ plus $Li_2O \cdot SiO_2$ plus quartz at 1 to 2 Kb, $Li_2O \cdot SiO_2$ plus quartz at 5 to 20 Kb and $Li_2O \cdot SiO_2$ plus coesite at 30 Kb. Crystallization of the glass at atmosphric pressure was observed only on the runs made at 600°C. The crystallized product was lithium disilicate as already reported in the literature[6].

Instead of using the $Li_2O \cdot 2SiO_2$ glass as the starting material, in some experiments, the $Li_2O \cdot 2SiO_2$ crystal, which was prepared by heating the $Li_2O \cdot 2SiO_2$ composition glass at 600°C at atmospheric pressure, was subjected to the pressure of 20 and 30 Kb at 550°C. The resulting products were the same as those obtained from the glass of the $Li_2O \cdot 2SiO_2$ composition at the same temperature and pressure conditions: This result indicates that under such pressure and temperature the $Li_2O \cdot SiO_2$ crystal and the silica crystal (quartz or coesite) are equibrium products of the $Li_2O \cdot 2SiO_2$ composition.

(b) Glasses of the Compositions other than $Li_2O \cdot 2SiO_2$

The results obtained with the glasses of the compositions SiO_2, $Li_2O \cdot 4SiO_2$, and $Li_2O \cdot 1.5SiO_2$ are summerized in Table 2.

Table 2. Crystallization of SiO_2, $Li_2O \cdot 4SiO_2$ and $Li_2O \cdot 1.5SiO_2$ glasses under various high pressures (duration of compression was 20 min. with exception specially noted).

Starting material	Pressure (Kbar)	Temperature (°C)	Water	Product*
SiO_2 glass	30	500	with	Glass
	30	500 (for 90 min)	with	C
silica gel	30	500	with	C
$Li_2O \cdot 4SiO_2$ glass	0.001 (atm. pressure)	550	without	Glass
	0.001	600	without	L2S
	20	500	without	Glass
	20	500	with	Q+LS
	20	550	with	Q+LS
	30	550	with	C+Q+LS
	30	650	with	C+Q+LS
$Li_2O \cdot 1.5SiO_2$ glass	0.001	500	with	Glass
	0.001	550	with	Glass
	0.001	600	with	LS+L2S
	20	500	without	Glass
	20	500	with	LS+C+Q
	20	550	without	LS+C+Q
	30	500	without	LS+C+Q

* L2S; Lithium disilicate ($Li_2O \cdot 2SiO_2$) LS: Lithium metasilicate ($Li_2O \cdot SiO_2$)
Q: Quartz (SiO_2) C: Coesite (SiO_2).

The results with the $Li_2O \cdot 4SiO_2$ glass are similar to those for the $Li_2O \cdot 2SiO_2$ glass described above: Although the glass did not crystallize up to 600°C at atmospheric pressure, it crystallized at the temperature as low as 500°C when the pressure of 20 Kb was applied in the presence of water. The crystals precipitated were the $Li_2O \cdot SiO_2$ crystal and quartz.

The results with the $Li_2O \cdot 1.5SiO_2$ were also almost similar to those described above: The $Li_2O \cdot SiO_2$ and silica crystals (quartz and coesite) precipitated at above 20 Kb and above 550°C in the absence of water, and at above 20 Kb and above 500°C in the presence of water. At atmospheric pressure the crystals identified as the $Li_2O \cdot 2SiO_2$ precipitated barely from 600°C in the presence of water.

Conversion of silica glass to coesite crystal was found to occur when compressed at 30 Kb at the temperature of 500°C for 90 min. A run made using silica gel as a starting material showed that it converts to coesite much faster (20 min.) than the silica glass at the same pressure and temperature condition.

Conversion of High Pressure Phases at Atmospheric Pressure

The mixtures of lithium metasilicate plus coesite and lithium metasilicate plus quartz, which had been obtained by subjecting the $Li_2O \cdot 2SiO_2$ glass to 550°C and 30 Kb and to 550°C and 10 Kb, respectively in the foregoing experiments, were

Table 3. Changes of high-pressure crystalline phases by heating at atmospheric pressure.

High pressure phase	Heating		Result*
	Temperature	Time	
$Li_2O \cdot SiO_2$+Coesite	600°C	40 hr.	No change
	650	40 hr.	No change
	700	300 min.	No change
	750	300 min.	LS+Q+C
	800	100 min.	LS+Q+C
	850	10 min.	LS+Q
	900	30 min.	LS+Q+L2S
$Li_2O \cdot SiO_2$+Quartz	800	100 min.	No change
	850	100 min.	No change
	900	30 min.	LS+Q+L2S
	900	600 min.	L2S+LS+Q
	950	60 min.	L2S
Coesite	550	40 hr.	No change
	650	60 min.	No change
	750	60 min.	No change
	800	60 min.	No change
	850	60 min.	No change
	900	60 min.	No change
	950	60 min.	No change
	1000	60 min.	Coesite disappeard
	1050	60 min.	Coesite disappeard

* L2S: Lithium disilicate ($Li_2O \cdot 2SiO_2$) LS: Lithium metasilicate ($Li_2O \cdot SiO_2$)
Q: Quartz (SiO_2) C: Coesite (SiO_2).

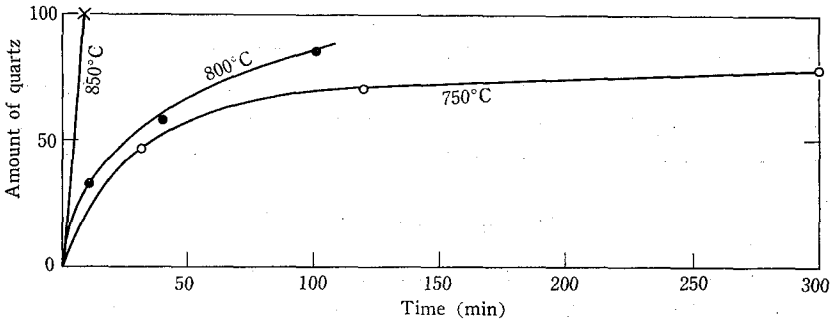

Fig. 3. The conversion, $Li_2O \cdot SiO$ + coesite ⟶ $Li_2O \cdot SiO_2$ + quartz at atmospheric pressure.

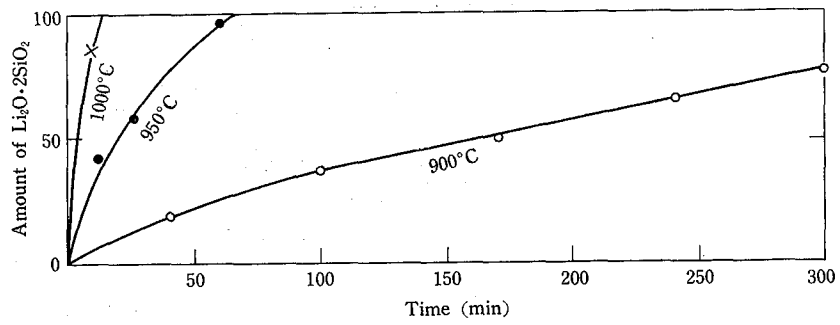

Fig. 4. The conversion, $Li_2O \cdot SiO_2$ + quartz ⟶ $Li_2O \cdot 2SiO_2$ at atmospheric pressure.

heated in the air (at atomospheric pressure) and at temperatures over 600°C for various times, and the resulting materials were subjected to the X-ray diffraction analyses. The results are given in Table 3, Fig. 3 and Fig. 4. The same experiment was carried out on the coesite crystals prepared in the foregoing experiment by subjecting the silica glass to 30 Kb and 500°C for more than 90 min.. Its result is also given in Table 3. Fig. 3 and Fig. 4 show the changes in ratio of the amount of original crystal in the samples e. g., coesite, to that of the converted crystal e. g., quartz, with time at various temperatures. The change in amount of the crystals was determined by measuring the height of the characteristic peaks of the crystals in their X-ray diffraction patterns.

From Table 3 it can be seen that the coesite in the mixture of the $Li_2O \cdot SiO_2$ crystal plus coesite starts to convert to quartz from 750°C, completing its conversion at 850°C. Conversion of coesite alone to quartz, the prosess of which is also given in Table 3, is sluggish i. e., the coesite remained almost unchanged up to 950°C. This indicates that the conversion of coesite is fascilitated by the presence of lithium metasilicate. The high stability of pure coesite at atmospheric pressure was already reported by Zeto, Dachille and Roy[2].

The mixture of the $Li_2O \cdot SiO_2$ crystal plus quartz remained unchanged up to 850°C, began to convert partly from 900°C and completely at 950°C to the $Li_2O \cdot 2SiO_2$ crystal.

From Fig. 3 and Fig. 4, the activation energies for the conversions were calculated using an equation,

$$E = K(1/T_1 - 1/T_2)^{-1} \log (r_2/r_1)$$

where r is the initial rate of conversion obtained approximately from tangents drawn to the conversion-time curves, and T is the absolute temperature. Their values were 0.9 kcal/mole for $Li_2O \cdot SiO_2$ + coesite $\longrightarrow$ $Li_2O \cdot SiO_2$ + puartz at 750° to 800°C and 5 kcal/mole for $Li_2O \cdot SiO_2$ + quartz $\longrightarrow$ $Li_2O \cdot 2SiO_2$ at 900° to 950°C.

IV. SUMMARY AND DISCUSSION

The results of the present experiments may be summerized as shown in Fig. 5 and Fig. 6. Arrows in Fig. 5 given directions of transformation of the $Li_2O \cdot 2SiO_2$ composition in the given conditions for temperature and pressure. As

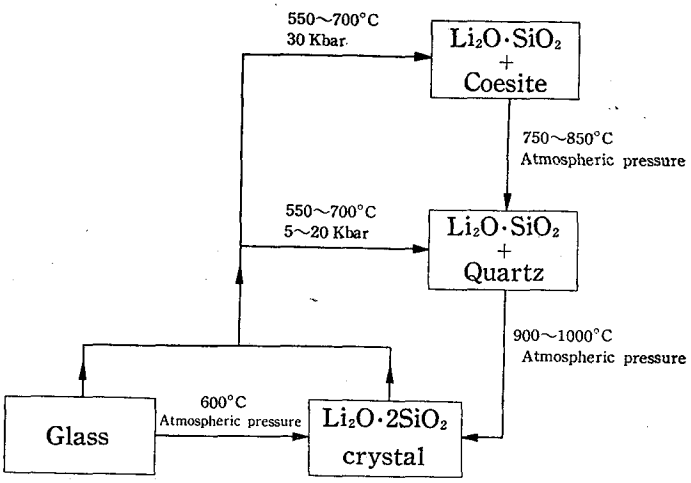

Fig. 5. Crystallization of $Li_2O \cdot 2SiO_2$ glass and transformation of the crystallized products.

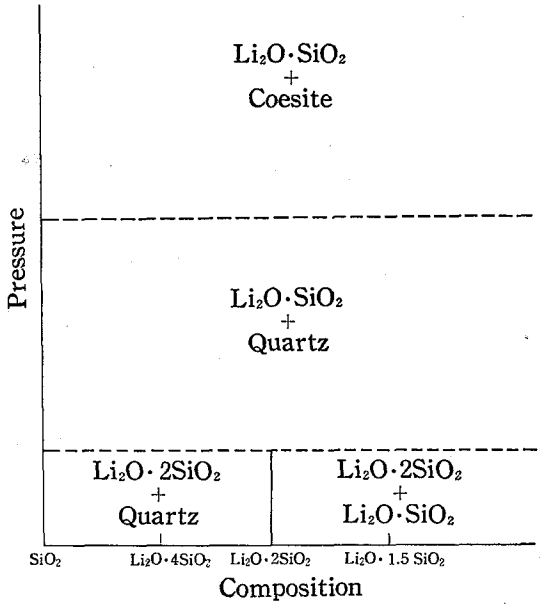

Fig. 6. Tentative diagram for the system Li_2O-SiO_2.

shown in both figures, lithium disilicate crystal is not stable at high-pressure and decomposes to lithium metasilicate and silica (quartz or coesite). The higher stability of the mixture, lithium metasilicate and silica, at high-pressure can be explained on the basis of their molar volumes which are listed in Table 4. The phase transformation under high-pressure proceeds in such a direction that the total molar volume of the phase decreases. The transformation, $Li_2O \cdot 2SiO_2 \longrightarrow Li_2O \cdot SiO_2 + quartz$, is therefore understandable because the total molar volume decreases from 61.2 to 58.4 cm^3.

Table 4. Density and molar volume of the crystals.

Crystal	Density[9] $d(g/cm^3)$	Molar Volume $V=M/d$ (cm^3)
$Li_2O \cdot 2SiO_2$	2.454	61.2
$Li_2O \cdot SiO_2$	2.520	35.7
SiO_2 (Quartz)	2.650	22.7
$Li_2O \cdot SiO_2 + SiO_2$ (Quartz)		58.4

The effect of high-pressure in accelerating the crystallization of glass or the phase transformation between two crystals can be explained, if the pressures applied involve a high degree of shear.

As described previously, the pressure apparatus used in the present experiment is of uniaxial type which generates the pressure involving a high degree of shear. The reconstruction of the glass or the crystal structure would be fascilitated by the shearing force.

The effect of water in accelerating the crystallization of glass under high-pressure, which was already estabilishd with some other glasses by Roy et al, was also found to be noticeable with the glasses investigated in the present work. To its reasoning W. A. Weyl's screening theory[10] would be feasible to be applied. "The addition of water to a silicate system can best be described as the addition of O^{2-} ions which increase its anion to cation ratio and of protons which can move from one O^{2-} ion into the electron cloud of the others. By temporarily lowering the anionic charge the proton weakens the binding forces between silicon and oxygen ions: $Si^{4+}O^{2-}Si^{4+} \xrightarrow{H^+} Si^{4+}(OH)^-Si^{4+}$" and thus the conversion of glass to crystal would be facilitated.

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